UNIVERSITY OF PENNSYLVANIA

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A THESIS

IN BOTANY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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THE EFFECTS OF SULFUR DIOXID UPON PLANTS: METHODS OF STUDY

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The contamination of the atmosphere with sulfur dioxid has long been thought a detriment to the growth of plants as well as to the health of man. The supposedly harmful effects of the gas have been responsible for frequent litigation between farmers and foresters on the one hand and smelters and manufacturers on the other. The problem of the determination of such effects is of particular interest wherever smoke accompanied by sulfur dioxid is emitted from furnaces, coke ovens, or other combustion systems.

The original purpose of the writer was to study the effects of sulfur dioxid upon vegetation. It was soon found that known methods of experimentation were subject to certain errors, and that many problems in the method of conducting an experiment must first be solved. This work is therefore a study of method; it will probably be continued by applying the method developed to a study of the effects upon plants of air contaminated with traces of sulfur dioxid.

Historical Review

Methods for investigation of the effects upon vegetation of air contaminated with sulfur dioxid have been varied. Wislicenus, in 1897, determined sulfur dioxid by suspending in the air cotton saturated with barium carbonate to absorb sulfurous and sulfuric acids. After five to seven months the cotton was collected and the absorbed substances were determined. Weiler (1906) analyzed air by drawing 1,000 to 2,000 liters through potassium carbonate over a period of six hours, and the sulfur dioxid absorbed was weighed, after oxidation and precipitation, as barium sulfate; later Weiler substituted alkaline bromine water for potassium carbonate. Lunge (1899) used sodium hydroxid as an absorption fluid. After the absorption, one half of the solution was treated with barium chlorid to precipitate sulfur trioxid, and after addition of bromine water the other half was similarly treated to precipitate both sulfur dioxid and trioxid.

Among others who used gravimetric methods for air analysis were Gerlach (1909), who used potassium carbonate with bromine as the absorption fluid, Herbig (1909), who used a sodium hypobromite solution, and Ebaugh (1907), who drew air through an iodine solution. Gallagher (1909) used a hydrogen peroxid solution. Ascher and others (1908) drew filtered

air through potassium iodid, and later substituted hypo-iodous acid to which iodine crystals had been added for potassium iodid.

Ost (1899) drew 34.5 liters of smoke containing sulfur dioxid through a 0.1 *N* iodine solution in four and one half hours; after absorption, one half of the solution was titrated with 0.1 *N* thiosulfate and the remainder was treated with barium chlorid. Lehmann (1893) used 0.025 *N* iodine solution and 0.025 sodium thiosulfate solutions for large volumes of samples. Frazer (1907) used barrels fitted with cloth diaphragms, which were saturated with alkali carbonate; by the increase in the weight of the cloth the quantity of sulfur trioxid absorbed was determined. Reich (1917) determined the percentage of sulfur dioxid in air by finding the size of the sample needed to decolorize one cubic centimeter of iodine solution of known concentration; the Reich apparatus used a rubber stopper near the solution. Seidell and Meserve (1914) analyzed the air of railway tunnels by allowing a sample of air to rush into a partially evacuated flask containing a dilute starch solution, to absorb the mixture; the starch solution was then titrated with 0.001 *N* iodine solution. Holmes, Franklin, and Gould (1915) made air analyses by allowing a sample of air containing sulfur dioxid to rush into a partially evacuated flask containing a dilute starch solution; after absorption, the solution was titrated back to the color of a "blank" by means of a 0.001 *N* iodine solution. Rubber stoppers were used on these flasks.

Among those who conducted controlled experiments for a study of the problem was Wislicenus (1898) who exposed plants to sulfur dioxid obtained by burning known amounts of carbon bisulfid mixed with alcohol to a definite volume. The concentration of sulfur dioxid in the resulting air was calculated by the rate of burning of the carbon bisulfid-alcohol mixture. Later (1914) he liberated a stream of sulfur dioxid from a cylinder into the gas chamber; he used a 0.01 *N* solution of chromic acid as an absorption fluid to determine the concentration of the gas. Haywood (1905) conducted experiments according to the early methods used by Wislicenus. Kastle and McHargue (1907) determined the sulfur dioxid obtained in an air mixture by burning 0.1 gram portions of sulfur, using 0.1 *N* iodine and sodium thiosulfate solutions; they used comparatively large volumes of samples. Stoklasa (1923) exposed plants to sulfur dioxid obtained by burning a mixture of carbon bisulfid and alcohol. No method of analysis of the air for its sulfur dioxid content is described, although it is stated that the mixture analyzed had a lower concentration of gas than that calculated from the weight of the carbon bisulfid burned.[1]

General Statement as to Equipment

The equipment used in the early experiments herein described differed from that employed in the later ones as various improvements were adopted from time to time. The final apparatus only is here discussed. The gas

[1] Since the above was written, a letter has been received from Dr. Stoklasa stating that the gravimetric method of determining the concentration of sulfur dioxid was used.

chamber used throughout the investigations was built in a greenhouse. It was enclosed by double sashes, and all joints, after being tightly sealed with putty and paint, were covered with shellac, a treatment that was necessarily repeated at frequent intervals. The chamber was 2.1 meters long and 0.67 meter wide; the top sloped toward the south, giving a height at the front of 1.3 meters and at the back of 0.95 meter, with a capacity of 1,610 liters. The chamber had two tightly fitting doors, one opening into the greenhouse and the other out of doors; the door into the greenhouse had a circular opening about 10 inches in diameter, devised to enable the investigator to reach into the case without loss of sulfur dioxid. The opening was carefully sealed with a piece of sheet rubber with the center cut sufficiently to fit tightly about the wrist when a hand was put through the opening; when not in use the hole in the rubber was kept closed by means of a Hoffman clamp. The opening was further fitted with a wooden disc, gasketed with a felt strip which insured against leakage. The chamber was equipped with a wet-and-dry-bulb psychrometer, and with an electric fan to mix the gas; the blades of the fan were coated with shellac.

The investigations herein discussed were carried on in the botanical laboratories of the University of Pennsylvania and covered the period of time from October, 1922, to July, 1924.

The writer wishes to express her sincere appreciation to Dr. R. H. True for the stimulus of his untiring interest and generous assistance throughout the work. Acknowledgment and thanks are expressed to Dr. W. D. Langley for his active interest and valuable suggestions; to Dr. W. R. Taylor for his generous aid and advice given in the preparation of the plates and the text figures; and to Dr. C. H. Arndt for valuable criticisms of methods and apparatus.

Methods of Generating Sulfur Dioxid

From Sulfur. In the early investigations, arsenic-free sulfur, calculated to give a desired concentration of sulfur dioxid, was weighed in a small crucible and burned within the gas chamber. It was found difficult to burn the small quantities which were to be used (*e.g.*, 0.0229 gram calculated to give a concentration of 0.001%, or 10 parts of sulfur dioxid in 1,000,000 parts of mixture). For complete combustion of the sulfur it was necessary to use an alcohol lamp to melt the sulfur before it was burned. Thus it was possible for acetaldehyde to be produced which, with the sulfur dioxid, seemed likely to produce a different effect upon plants from that produced by sulfur dioxid alone. Consequently an attempt was made to bring an electrically heated coil of platinum wire in direct contact with the sulfur; it was found difficult to control the resistance in the circuit, and as a result the wire fused. Further, some sulfur trioxid, in addition to sulfur dioxid, was produced by this method and it was therefore abandoned.

The sulfur was next burned by being placed upon the bottom of an inverted Pyrex beaker which was placed into a circular opening in the bottom of the chamber, over a heating unit from a commercial electric heater. The coil and beaker were insulated and surrounded with a 6-centimeter packing of asbestos cement. The inverted beaker served the three-fold purpose of (*a*) protecting the wire coil from the action of the sulfur dioxid, (*b*) of insulating the coil, thus avoiding a rise in temperature, and (*c*) of keeping the case tightly sealed. When an experiment was to be conducted, the current was turned on and the weighed sulfur, on thin platinum foil, was put on the inverted beaker. The gradual rise in temperature resulted in the production of some sublimed sulfur. Further sources of error in the method of burning sulfur were found to be: adsorption on the glass walls, absorption by the soil and other agencies, and a relatively rapid oxidation, so that the concentration of sulfur dioxid obtained was less than that expected from the amount of sulfur burned. The method of burning sulfur to obtain sulfur dioxid was therefore abandoned, and other means of generating the gas were employed.

From Sodium Bisulfite. A 10% solution of sulfuric acid was allowed to drop upon a saturated aqueous solution of sodium bisulfite, and the sulfur dioxid evolved was washed by being passed through another saturated aqueous solution of sodium bisulfite and sulfur dioxid. It was necessary to adapt apparatus for testing the purity of the sulfur dioxid, for collecting and measuring it, and for conducting it into the chamber where it was to be diluted with air before plants were exposed to it. The manipulation of the gas presented a number of difficulties caused by changes in volume due to changes in temperature and in pressure and by adsorption of the gas, as mentioned under the heading "Procedure for an Experiment." The apparatus, of which Plate IX is a photograph, is discussed under three headings, namely, the generating apparatus, the gas chamber, and the apparatus for withdrawing and analyzing the sample.

The generating apparatus (*a* to *p*, Pl. IX) consisted of a one-liter Erlenmeyer flask, *a*, placed in a water bath, and containing a suspension of sodium bisulfite in water. It was fitted with a three-hole rubber stopper through which were inserted a separatory funnel, a tube with stopcock connected to the equilibrium flasks, *g* and *g'*, and a tube with stopcock to conduct the gas into the 500-cc. washing bottle, *h*, containing distilled water saturated with sodium bisulfite and sulfur dioxid. The inlet tube of this bottle was terminated by an aërating bulb. The outlet of the washing bottle led to a three-way stopcock, *i*, which was connected by one arm to a second three-way stopcock (seen back of *i*, Pl. IX), and by the other arm to the collecting cylinder, *l*. From the second three-way stopcock the gas could be sent either out of doors through the Y-tube, *k*, or to the testing cylinder, *a*.

The second arm of the first stopcock, *i*, which leads to the collecting cylinder, *l*, was connected to an inlet tube reaching nearly to the bottom of

the calibrated collecting cylinder filled with 800 cc. of water saturated with sulfur dioxid and sodium bisulfite. The outlet, *n*, from this cylinder led to an opening in the gas chamber, and a tube from an opening at the bottom of the cylinder was connected, by means of a shellacked rubber hose, to the bottom of a leveling flask, *m*, which was operated by a rope-and-pulley system. The rubber stopper in the top of the leveling flask had two holes, one fitted with an overflow tube leading from the bottom of the flask, so that only the surface of the column in the overflow tube came in contact with the outside air. The other hole was fitted with two U-tubes, in series, of which the first contained a mercury trap and the second sodium hydroxid to absorb any sulfur dioxid which escaped through the mercury of the first.

A safety device to control changes in pressure and volume was that of two 2-liter Erlenmeyer flasks, *g* and *g'*, connected in series between an outlet of the generator and one arm of the Y-tube, *k*, leading to the opening out of doors. With fluctuations of sulfur dioxid pressure in the generator, water saturated with both sulfur dioxid and sodium bisulfite moved from the first equilibrium flask to the second, and *vice versa*. In cases of excessive pressure, the tube from the second equilibrium flask conducted the excess gas out of doors. This device prevented the sucking back of the solutions in *h* and *l* into the generating flask, and also the sucking of air into the system when pressure or volume within decreased.

Apparatus for Gas Analysis

Gas Chamber. The chamber as described above was used throughout this work. During warm weather the top and outer sides were covered with white lead to diffuse the direct rays of the sun. The inner surface was later coated with paraffin. The reason for these steps will be found under the heading "Behavior of Sulfur Dioxid in Contact with Glass."

Absorption Tubes. Three cylindrical absorption tubes connected in series (see *x* in Pl. IX, also text fig. 4) were joined by a stopcock, *v*, to the outlet, *u*, from the chamber. The tubes were fitted with ground-glass stoppers having three openings: an inlet tube terminated with an aërating bulb leading under the surface of the iodine solution, an outlet leading to an aspirator, and an opening, *a*, fitted with a ground-glass stopper, by means of which the excess iodine could be titrated *in situ*. The tubes were 45 cm. long, and 3.4 cm. in outer diameter.

Aspirating Apparatus. The absorption tubes, *x*, were connected to a 12-liter aspirating bottle, *B*, to which was also connected, by means of a rubber hose at the bottom, a 6-liter graduated measuring flask, *F*, with long neck and bulb, for the purpose of leveling, or of obtaining atmospheric pressure in both the aspirator and the measuring flask. A wooden crate, *G*, attached to rope and pulleys, enabled the leveling bottle to be raised or lowered. A glass tube, *y*, connected in parallel with the absorption tubes

between the stopcock, *v*, and the T-tube leading to the 12-liter aspirator, *B*, provided means for washing air from the system before drawing the sample; for the same reason a second opening, at the bottom of the aspirator, *B*, served to draw water through the tube *E*, not connected to the measuring-flask.

Solutions. The solutions used in the analyses were a 0.001 *N* iodine solution containing two hundred grams of potassium iodid per liter of solution; a 0.001 *N* solution of sodium thiosulfate, prepared with freshly boiled distilled water. Various concentrations of the above-mentioned solutions ranging from 0.02 *N* to 0.001 *N* were tried, and the last-named proved to be the most satisfactory. It was carefully standardized to avoid error that is likely to result by diluting tenth- or hundredth-normal solutions. A starch solution containing one gram of soluble starch per liter of water, made fresh every day, was used as an indicator for the titration.

Procedure for an Experiment

Generating Sulfur Dioxid. Dilute sulfuric acid was dropped from the separatory funnel upon the saturated solution of sodium bisulfite which was warmed by means of a water bath. Occasional shaking of the generating flask was necessary to facilitate the production of gas at a uniform rate. The chemical reaction which occurred was:

$$2NaHSO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2SO_2 + 2H_2O.$$

The sulfur dioxid was washed in the washing bottle, *h;* it was sent out of doors *via i, j, k* until it was thought to be free of air, when the stopcock, *i*, was turned so as to send the sulfur dioxid into a cylinder, *a*, containing a sodium hydroxid solution. A tube filled with sodium hydroxid from the cylinder was inverted over the small tip of the tube, *b;* if the bubbles of sulfur dioxid coming into the inverted tube were completely absorbed, *i.e.*, if sodium hydroxid was not forced out of the inverted tube, the sulfur dioxid was known to be free from air. The stopcocks were then turned so as to send the gas into the collecting cylinder, *l*, containing water saturated with sulfur dioxid and sodium bisulfite. The sulfur dioxid entering the cylinder forced the level of the liquid down, sending it through the connecting hose at the bottom into the leveling bottle, *m*. In practice, the gas was collected under a pressure of several centimeters of water. When the volume was to be read, the gas was brought to atmospheric pressure by lowering the leveling bottle and the desired quantity of gas was sent into the chamber, *g;* with the stopcock, *i*, closed and the one between *l* and the chamber open, by means of the rope-and-pulley system, *p*, the leveling bottle was slightly raised, thus forcing the gas through the tube, *n*, into the chamber.

Thermometer and barometer readings were taken to furnish data necessary for making corrections in the volume of the gas. It was also

found necessary to make a correction for absorption of sulfur dioxid in the collecting cylinder during the short period that the gas was being forced from *l* into the chamber. This correction was necessitated since changes in temperature made it practically impossible to maintain equilibrium between gaseous and dissolved sulfur dioxid in the collecting cylinder; in the lower temperature of the morning the water dissolved sulfur dioxid, and evolved it as the temperature rose. For intervals of time during which the temperature varied but little, the sulfur dioxid was absorbed at a constant rate. By observing the rate of absorption for ten minutes immediately before sending the gas into the chamber, then observing the length of time used for moving the gas, the correction in the volume of gas used was easily made. In order to mix the gas, the electric fan within the chamber, near the inlet for the sulfur dioxid, was started shortly before the gas entered the chamber.

Analysis of the Mixture in the Gas Chamber

At 15- or 20-minute intervals analyses of the concentration of the mixture in the chamber were made. A sample of the mixture was drawn from the chamber through the tube, *u*, in less than four minutes, as water was drawn from the aspirator, *B*, into the collecting flask, *F*, fully a meter below the level of *B*. Before drawing the sample through the solution it was necessary to remove air from the system. The stopcocks *v* and *z* were turned so as to draw air or mixture through the tube *y*, while water was allowed to flow from the aspirator through the tube *E*. The air having been removed, the flow of water through *E* was stopped and the stopcocks were turned to open the inlet to the series of absorption tubes, *x;* the sample was then drawn through the iodine and starch solutions in the series of tubes while water was being drawn from the aspirator into the measuring flask. When approximately six liters of water had been drawn, the measuring flask was raised by means of the rope-and-pulley system, *H*, and the water in the flask was leveled with that in the aspirator. The quantity of water drawn represented the volume of the sample minus the sulfur dioxid removed. Corrections to standard conditions were made, and the result, added to the volume of sulfur dioxid removed (a negligible volume in these calculations) represented, quantitatively, the sample of the mixture drawn from the chamber. The first absorption tube (text fig. 4) through which the sample was drawn contained an accurately measured quantity of 0.001 *N* iodine solution, which quantity varied from 20 to 80 cc. according to the concentration of gas used; the second tube, of smaller diameter (18 mm.), contained 15 cc. of starch solution so as to enable the detection of any volatilization of iodine; such volatilization did not occur when the iodine solution contained the quantity of potassium iodid specified under "Solutions." When the concentration of sulfur dioxid was estimated to be sufficiently high to reduce a larger quantity of iodine than that contained

in the first tube, a second iodine tube was put behind the first. As the sample was drawn through the solution, the sulfur dioxid present reduced the iodine thus:

$$I_2 + 2H_2O + SO_2 \rightarrow H_2SO_4 + 2HI.$$

The excess iodine was titrated with 0.001 *N* sodium thiosulfate until the end-point was near, when the contents of the starch tube was added to the iodine and the titration with sodium thiosulfate was completed. The following reaction occurred:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI.$$

From the quantity of iodine reduced the sulfur dioxid content of the sample, hence of the chamber, was found. All calculations for these results were made as shown below:

Example: July 14

Water drawn, 5,990 cc.
Humidity in chamber, 38.3% (∴ 61.7% w.v.[2] added to sample).
Temperature:
Chamber, 41° C. (v.p.[3] = 57.98 mm.).
Absorption tubes, 32.5° C. (v.p. = 36.4 mm.).
Barometer, 759 mm.
Iodine reduced, 50.25 cc. (N.F. = 0.00093).
759 − 36.4 (v.p. in absorption tubes) = 722.6 mm. pressure.
$\frac{722.6}{759} \times 5{,}990 = 5{,}703$ (cc. gas mixture in sample).
5,990 − 5,703 = 287 (cc. w.v. at 100% humidity).
287 × 0.617 (61.7%) = 177.18 cc. (w.v. added to sample outside chamber).
5,990 − 177.1 = 5,812.9 (cc. in sample at 32.5° C., 759 mm.).
759 − [38.3 × 57.98 (v.p. at 41° C.)] = 736.8 mm. (g.p.[4] of sample in chamber).
$\frac{736.8}{759} \times \frac{273}{305.5} \times 5{,}812.9 = 5{,}042.5$ (vol. in cc. of sample minus SO_2 removed).
Iodine reduced = 50.25 cc. with N.F. of 0.00093
= 0.0467 cc. normal iodine reduced.
(1 cc. normal iodine = 0.0112 cc. sulfur dioxid (s.c.[5]).
0.0467 × 0.0112 = 0.5234 (cc. sulfur dioxid in sample).
5042.5 + 0.5234 = 5043.2 (cc. in total sample drawn).
0.5234 ÷ 5043.2 = 0.010379% SO_2
= 104 parts SO_2 per million parts of the mixture.

Sources of Error

Temperature. A direct effect of temperature is the difficulty of keeping the water in the collecting cylinder, *l*, and in the leveling bottle, *m*, saturated with sulfur dioxid. The absorption coefficient of sulfur dioxid by water at 760 mm., according to Freese, ranges thus:

	Temp.	Liters SO_2	G. SO_2
1 volume of water absorbs.....	0°	79.79	228.29
	20°	39.37	112.90
	40°	18.78	54.11

[2] w.v. = water vapor.
[3] v.p. = vapor pressure.
[4] g.p. = gas pressure.
[5] s.c. = standard conditions.

It is obvious, from the above figures, that the sulfur dioxid capacity of water in the collecting cylinder and in the leveling bottle changes as frequently and as continuously as the temperature changes, and that resaturation is repeatedly necessary. It was thought that a heavy mineral oil might be substituted for the water in these containers, with the hope that the solubility in such an inert substance might be very low. It was found, however, that during a period of 20 hours, 175 cc. of gas were absorbed. This rate of absorption, together with the fact that the time required to send sulfur dioxid into the case by oil-displacement was greater than the time required by water-displacement, proved the latter method the better one and it was again used. Corrections for absorption of sulfur dioxid by water are explained under "Procedure for an Experiment."

A third effect of temperature was to cause a variation in the concentration of sulfur dioxid in the chamber. This matter will be discussed in more detail under the heading "Behavior of Sulfur Dioxid in Contact with Glass."

Rubber Stoppers. In order to test air known to be sulfur dioxid-free it was washed by being drawn through a series of tubes containing an iodine solution, then immediately drawn through a second series similar to and directly connected to the first; if any sulfur dioxid was present in the sample of air, the iodine in the first series of tubes absorbed it, and there could be no gas present to reduce iodine in the second series; the iodine of each series was titrated separately.

TABLE I. *Tests of Outside Air (April 2)*

Trial	Cc. I_2 Used	Cc. I_2 Reduced	Min. for Drawing Sample	Cc. H_2O for Sample	Temp. °C.	Cc. SO_2 Found	SO_2 Found (Parts in Million)
I *a*	25.70	16.83	13	8,675	41.5	0.1652	19
I *b*	24.935	14.89				0.1460	17
II *a*	24.96	4.56	6.75	8,640	41.5	0.0448	5
II *b*	24.98	5.92				0.0581	6.7
III *a*	24.95	9.36	6	8,635	41	0.0918	10.6
III *b*	25.00	8.01				0.0786	9
IV *a*	24.96	14.265	21	8,120	39	0.1400	17
IV *b*	24.94	13.67				0.1341	16.5
V *a*	24.99	11.68	21.5	8,160	38.5	0.1145	14.4
V *b*	25.00	14.75				0.1445	17.7

Note. Six tubes were used in each set of trials: two series (*a* and *b*), each containing two tubes with iodine and one with potassium iodid.

Such tests showed that (*a*) the reduction of iodine in the second series of tubes in which the sample was known to be free of sulfur dioxid was as great as in the first series, and (*b*) the time used in drawing the sample had a relation to the quantity of iodine reduced.

At this stage of the investigations rubber stoppers were used for the absorption tubes, and it was thought that the loss of iodine which appeared to show the presence of sulfur dioxid was due to reduction by the rubber, although the rubber stoppers were fully ten centimeters from the solution. The idea was strengthened by the fact that there was an increase in the quantity of iodine reduced as the length of time for drawing the sample increased. A careful study of this point was made by making tests with outside air after having coated all rubber stoppers and connecting tubing with paraffin.

TABLE 2. *Rubber Stoppers and Tubing Coated with Paraffin (April 3)*

Trial	Cc. I_2 Used	Cc. I_2 — Equiv. of Titration	Min. for Drawing Sample	Cc. H_2O for Sample	Temp. ° C.	SO_2 — Found (cc.)	SO_2 — Found (%)
I *a*...	24.95	26.00	13	8,450	51.5	*Slight neg. value	Slight neg. value
I *b*...	24.90	26.82					
II *a*...	25.00	27.44	9.3	8,610	48.5	Slight neg. value	Slight neg. value
II *b*...	24.94	24.95					
III *a*...	25.00	28.31	8	8,610	45.5	Slight neg. value	Slight neg. value
III *b*...	24.97	28.28					

* Negative value is shown in that the iodine used is slightly less in quantity than the iodine-equivalent of titration. These negative values were later eliminated when neither distilled water nor potassium iodid was added to the iodine before titration. See discussion of this point under the heading "Variations in Solutions."

Table 2 shows that when rubber surfaces were coated with paraffin there was no reduction of iodine, and the fact is obvious that rubber had been reducing the iodine solutions, thus seeming to indicate the presence of sulfur dioxid. It was clear that the use of rubber must be eliminated, and therefore absorption tubes with ground-glass stoppers were used.

Variations in Solutions. In the early determinations for sulfur dioxid content, potassium iodid, instead of starch, was used in the last absorption tube; after the sample had been drawn through the solutions, both iodine and potassium iodid were poured into a beaker, and, in order to prevent loss of iodine, the tubes were carefully washed with distilled water or with potassium iodid; the titration of this diluted iodine was then carried out in the beaker. It was found that such dilution of iodine had an effect upon the relation of the sodium thiosulfate solution to the iodine solution, which relation varied as the quantities of distilled water and of potassium

iodid varied. It was therefore necessary to avoid these variations by replacing the potassium iodid in the third absorption tube by starch, and to carry out titrations directly in the absorption tubes; the ground-glass stopper of the absorption tube (see text fig. 4) was devised at this point.

A variation was also found in the ratio of the sodium thiosulfate to the iodine solution, which ratio decreased slightly from day to day. The following results are typical, and show that it was necessary daily to find the relation between the solutions:

June 20, $\frac{Na_2S_2O_3}{I_2}$ relation, 0.9878.
June 21, 0.9600.
June 23, 0.9568.
June 24, 0.9555.
June 25, 0.9507.

Accuracy of Method

The method is proven to be accurate to one part in a million and fairly accurate to two parts in ten million; the range of error is five parts in ten million.

The accuracy of the method, as found in blank tests, is shown in table 3.

TABLE 3. *Accuracy of Method (May 12)*

Trial		Cc. I_2 Used	Cc. I_2 Reduced	Min. for Drawing Sample	Cc. H_2O for Sample	Cc. I_2 Error	SO_2 — Equiv. of Error (Pts. per Million)
I	*a*....	24.93	24.964	7	5,800	+0.066	+0.123
	b....	24.85	24.852			−0.002	−0.004
II	*a*....	24.95	25.128	7	5,790	−0.178	−0.331
	b....	24.96	24.864			+0.096	+0.178

After the accuracy in the method of making determinations was established, it seemed desirable to determine the purity of the sulfur dioxid, as well as the degree of accuracy obtained in measuring the gas in the collecting cylinder. With these aims in mind, the absorption tubes, containing the iodine solution, were connected to the collecting cylinder, and the sample was sent directly from the collecting cylinder into iodine.

TABLE 4. *Purity and Accuracy in Quantity of Sulfur Dioxid (May 13)*

Trial	Cc. Sample SO_2* (Standard Conditions)	Cc. I_2 Used	Cc. I_2 Reduced	Temp. ° C.	Cc. SO_2 Determined	Cc. SO_2 Error
I....	38.20	47.76	34.52	20	38.28	0.08
II....	42.77	42.30	36.58	28	40.84	1.93

* No correction for vapor pressure.

The discrepancy shown between the quantity of sulfur dioxid in the sample and the quantity determined is within the limit of error in reading the volume of sulfur dioxid. As shown later in this paper, the quantity of gas sent into the chamber differs very much from the quantity found present in the chamber, and it is therefore not essential that the method of measuring the pure sulfur dioxid be absolutely accurate. On the other hand, it is very important that the method of determining the concentration of gas present have the greatest degree of accuracy.

Behavior of Sulfur Dioxid in Contact with Glass

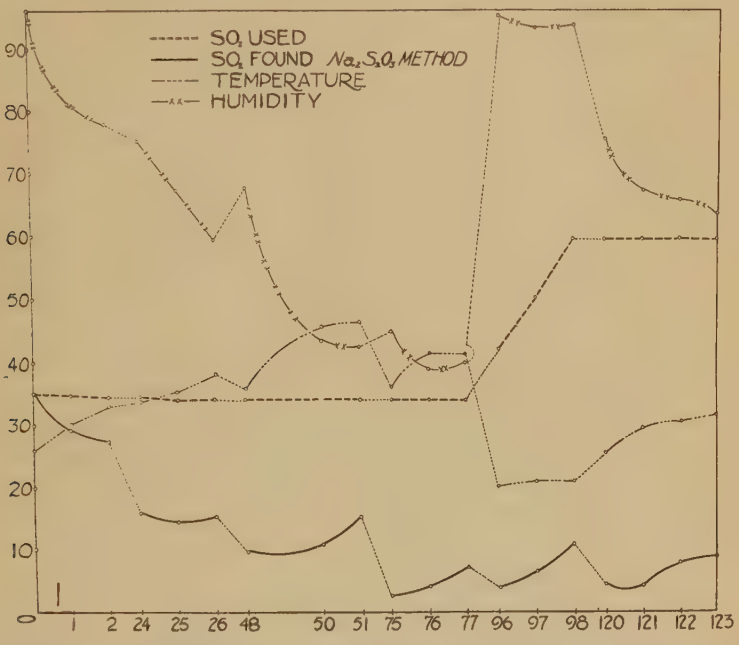
Interesting phases of the behavior of sulfur dioxid were presented in (*a*) the wide discrepancy between the quantity of gas sent into the chamber and the quantity determined immediately afterward; this difference is called the sulfur dioxid discrepancy; (*b*) the less rapid but continuous disappearance or loss of sulfur dioxid, and (*c*) the fluctuation in sulfur dioxid concentration with changes in temperature.

The relatively small amounts of sulfur dioxid determined immediately after a considerable quantity of gas had been sent into the chamber, and a further apparent loss or disappearance of a large proportion of the gas, an hour later, led to repeated checks on the accuracy of the method. The problem was first approached from the standpoint of possible leakage from the chamber. In order to determine whether this was a possible cause of the loss of sulfur dioxid, it was sent in large quantities from the collecting cylinder into a 19-liter carboy, from which the leakage was negligible. The carboy was well shaken immediately before a determination, so as to insure mixing of the gas. The results obtained were but slightly more uniform than those obtained from the chamber. After repeated determinations having similar results, it was certain that the leakage of gas from the chamber was not the causal factor of the sulfur dioxid discrepancy, or of the later disappearance of the gas.

A careful study of this behavior, with repeated experiments in the carboy and in the chamber, showed that the adsorption of sulfur dioxid on surfaces, and oxidation, both being influenced by temperature, and perhaps other possibilities, are the controlling factors in regulating the sulfur dioxid content of the air-gas mixture. The sulfur dioxid discrepancy was often as much as 75% of the gas used (see fig. 3), and its further gradual loss, with duration of time, was such that a second test, one hour after the first, frequently showed but 50% of the first determination. Fluctuations often appeared, so that certain determinations showed a higher sulfur dioxid content than previous tests in the same series, although some of the gas must have been oxidized in the meantime.

Adsorption. The inside walls of the glass chamber presented a large glass surface, on which the gas, upon entering the chamber, was adsorbed and inactivated, thus very considerably reducing the diffusible gas which could be drawn for analysis.

There was evidence that adsorption of sulfur dioxid gradually approached a maximum, which point may be called the "saturation equilibrium"; this was shown by the fact that the sulfur dioxid discrepancy was invariably much greater in the first determination following a period when the gas content of the chamber was low. The sulfur dioxid discrepancy decreased after large quantities of gas had been used for a number of consecutive days, but saturation of the glass was apparently difficult to obtain, and was of short duration (see text figs. 1, 2, 3).

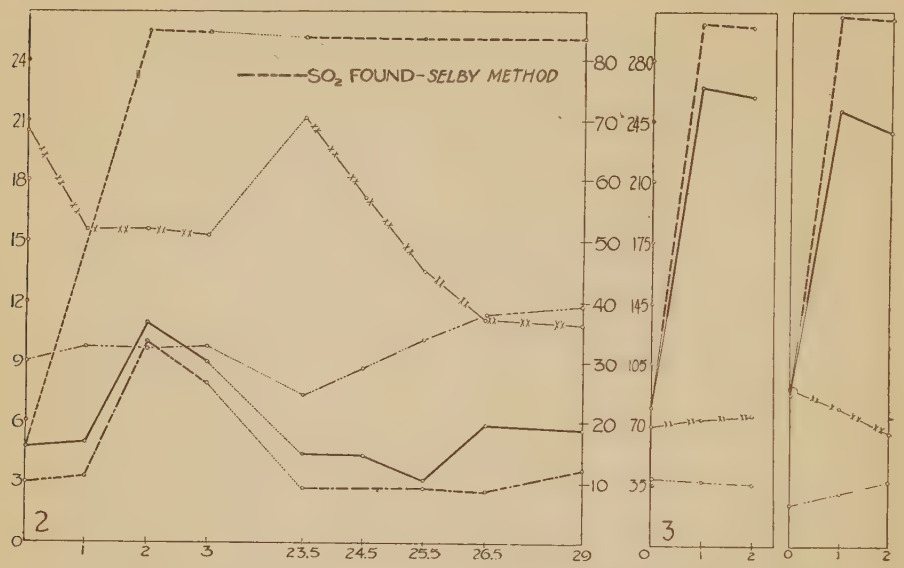


TEXT FIG. 1. Discrepancy, loss, and fluctuations of sulfur dioxid, June 23–28. Ordinates: sulfur dioxid in cc.; temperature in degrees C., and humidity in percentages. Abscissae: time in hours. . . ., interval of time during which no analyses were made.

The sulfur dioxid discrepancy decreased markedly when glass surfaces were eliminated by having the inside walls of the chamber coated with paraffin.

Oxidation of Sulfur Dioxid to Sulfuric Acid. Besides the loss of sulfur dioxid due to adsorption, there was a further loss due to oxidation from sulfur dioxid to sulfur trioxid. This was proved by the formation of a precipitate of barium sulfate from a neutral solution of barium chlorid put into the chamber; the precipitate was shown to be barium sulfate, and not barium carbonate, by its insolubility in nitric acid. The beaker containing the barium chlorid had been coated with paraffin, so that oxidation by catalysis was reduced to a minimum. The process of oxidation was found to be less rapid after the inside of the chamber was coated with paraffin,

indicating that oxidation, as well as adsorption, is less active in contact with a paraffin than with a glass surface.



TEXT FIG. 2. Comparison of $Na_2S_2O_3$ and Selby methods, July 2, 3. Ordinates to left of figures, sulfur dioxid in cc.; ordinates to right of figures, temperature in degrees C. and humidity in percentages. Abscissae and . . . as in text fig. 1. The lowest curve is for the Selby method. Explanation of other curves as in text fig. 1. TEXT FIG. 3. Discrepancy and loss of sulfur dioxid, June 20, 21. Ordinates, abscissae, and . . . as in text fig. 1. Explanation of curves as in text fig. 1.

TABLE 5. *Results for Glass Surface (May 2)*

Trial	Temp.	Cc. SO_2 Used	Cc. SO_2 Determined	% SO_2 Determined	% SO_2 Lost
I....	25.6	268.75	174.68	65	35
II....	24	none	139.66	52*	48
			Results for Paraffin Surface (June 18)		
I....	32.3	227.0	223	98	2
II....	30.4	none	195	85†	15

Note. The higher temperature of June 18 tends to give a somewhat higher percentage in concentration, but it does not account for the total increase over May 2; the greater increase is due to the less rapid rate of adsorption and of oxidation in contact with a paraffin than with a glass surface.

* 80% of trial 1.

† 86.7% of trial 1.

Temperature and humidity are important factors influencing the adsorption and the oxidation processes discussed above, and therefore have

a great effect in determining the percentage of sulfur dioxid obtained in an analysis. A study of the fluctuations, which frequently showed by a higher sulfur dioxid content in certain tests than in previous ones of the same series, proved that at high temperature and low humidity there is less

TEXT FIG. 4. Absorption tube × about ⅛. Closely fitting ground-glass stopper has three openings: (1) inlet, (2) opening, *a*, for titration purposes, and (3) outlet. Length of tube, 45 cm.; outside diameter, 3.4 cm.; span of arms, 10.5 cm.

adsorption on surfaces and a less rapid rate of oxidation than at low temperature and high humidity (see text figs. 1, 2, 3). A coat of lime on the top and outer sides of the chamber, to diffuse the sunlight, reduced the range in temperature variation and therefore the range of fluctuation in concentration of the gas.

COMPARISON OF THE METHOD DEVELOPED WITH THE METHOD USED BY THE SELBY SMELTER COMMISSION

The method used by the Selby Smelter Commission in California was compared with the method herein discussed and was found to be less accurate. The report of this commission, published by the Bureau of Mines in 1915, describes their method which consisted primarily in the use of two 24-liter aspirating bottles, each containing 250 cc. of fresh starch solution; one aspirator was evacuated to a 380-mm. vacuum; the other one, not evacuated, was used for a "blank" or control determination. The sample of sulfur dioxid-air mixture was taken by opening a stopcock of the evacuated aspirator and allowing the mixture to rush into the flask,

thereby bringing the pressure within the aspirator back to atmospheric pressure. After both aspirators had been shaken vigorously so as to have the sulfur dioxid of the sample absorbed by the iodine, the solution from each aspirator was transferred to a 500-cc. test bottle; the colors of the solutions were compared, and sufficient 0.002 *N* iodine solution was added to the solution containing the sample to bring the color to that of the control. The quantity of iodine needed to obtain the required color represents the quantity reduced by the sulfur dioxid, and with these figures the gas content of the volume drawn into the aspirator was calculated.

Plate IX shows the arrangement of apparatus as used in these comparative determinations. The outlet, *u*, from the gas chamber is connected to both the aspirator, *w*, and the absorption tubes, *x*, by means of the three-way stopcock, *v;* the aspirator, evacuated to 380 mm., receives the sample for determination according to the Selby method; the absorption tubes, *x*, receive the sample for determination according to the thiosulfate method. The samples are taken simultaneously, since the mixture drawn from the chamber is divided at *v* between the two arms leading respectively to the partially evacuated aspirator and to the absorption tubes. The second aspirator, *w'*, is the one containing the "blank" solution.

Many determinations, both separately and in parallel, were made with these methods for the purpose of acquiring sufficient skill in manipulation before any data or results were accepted as being significant. The comparative determinations reported were made at hourly intervals.

Comparative determinations were made with concentrations of sulfur dioxid ranging from 1.4 to 181 parts per million parts of air-gas mixture. A summary of the comparative analyses shows the following results:

Number of tests showing more SO_2 with $Na_2S_2O_3$ method	40.
Number of tests showing more SO_2 with Selby method	3.
Number of tests equal or doubtful [6]	2.

Text figure 2 charts the results of the comparative determinations of July 2 and July 3, and shows that determinations made with the sodium thiosulfate method indicate the presence of more sulfur dioxid than those made with the Selby method. From the results of these comparisons it seems certain that some of the sulfur dioxid is lost when determinations, in very dilute mixtures of the gas, are made according to the Selby method. The percentage of this error probably increases with dilution, since the quantity of sulfur dioxid lost on the large surface of the aspirator represents a greater percentage of loss in small quantities of sulfur dioxid than in large quantities of the gas.

It is reasonable to believe that the Selby method offers probable sources of error in (*a*) failing to correct for vapor pressure in the sample taken,

[6] Selby results higher than sodium thiosulfate if former are corrected for vapor pressure. Selby results lower than sodium thiosulfate if former are not corrected for vapor pressure.

TABLE 6. *Comparative Tests Made by Sodium Thiosulfate and Selby Methods*

Trial	Method	Temp. (° C.)	Humid. (%)	Barom. (mm.)	% SO_2 Determined	Parts SO_2 per Mill.
June 23						
I..	$Na_2S_2O_3$	26	96.4	762	0.002183	21.8
	Selby *a**	26	96.4	762	0.002095	21.0
	b†	26	96.4	762	0.002022	20.2
II..	$Na_2S_2O_3$	30	81.0	762	0.001808	18.0
	Selby *a*	30	81.0	762	0.001968	19.7
	b	30	81.0	762	0.001883	18.8
III..	$Na_2S_2O_3$	33	77.7	762	0.001697	17.0
	Selby *a*	33	77.7	762	0.001639	16.4
	b	33	77.7	762	0.001557	15.6
June 24						
I..	$Na_2S_2O_3$	33.9	75.0	761	0.000983	9.8
	Selby *a*	33.9	75.0	761	0.000749	7.5
	b	33.9	75.0	761	0.000713	7.1
II..	$Na_2S_2O_3$	35.3	67.2	761	0.000885	8.9
	Selby *a*	35.3	67.2	761	0.000841	8.4
	b	35.3	67.2	761	0.000796	8.0
III..	$Na_2S_2O_3$	38.3	59.2	761	0.000942	9.4
	Selby *a*	38.3	59.2	761	0.000743	7.4
	b	38.3	59.2	761	0.000699	7.0
June 25						
I..	$Na_2S_2O_3$	35.9	67.8	758.5	0.000599	6.0
	Selby *a*	35.9	67.8	758.5	0.000487	4.9
	b	35.9	67.8	758.5	0.000460	4.6
II..	$Na_2S_2O_3$	45.5	43.3	756	0.000651	6.5
	Selby *a*	45.5	43.3	756	0.000530	5.3
	b	45.5	43.3	756	0.000483	4.8
III..	$Na_2S_2O_3$	46.4	42.2	756	0.000941	9.4
	Selby *a*	46.4	42.2	756	0.000605	6.1
	b	46.4	42.2	756	0.000437	4.4
June 26						
I..	$Na_2S_2O_3$	36	44.7	761.5	0.0001430	1.43
	Selby *a*	36	44.7	761.5	0.0000106	0.11
	b	36	44.7	761.5	0.0000100	0.10
II..	$Na_2S_2O_3$	41	38.6	761	0.0002360	2.36
	Selby *a*	41	38.6	761	0.0000638	0.64
	b	41	38.6	761	0.0000593	0.59
III..	$Na_2S_2O_3$	41	39.7	761	0.0004275	4.28
	Selby *a*	41	39.7	761	0.0001463	1.46
	b	41	39.7	761	0.0001359	1.36

* Vapor-pressure corrections made in tests *a*.

† Vapor-pressure corrections not made in tests *b*.

(*b*) difficulty in maintaining a partial vacuum in the aspirator, (*c*) water vapor in the aspirator probably not acting according to Boyle's law, (*d*) rubber stopper, used in the neck of the aspirator, reducing the iodine, and (*e*) loss of sulfur dioxid and iodine on the large glass surface of the aspirator.

Summary

In studying the effects of sulfur dioxid upon vegetation it was found that methods of determination of the low concentrations of gas causing minimal injury to plants were unsatisfactory. Any method for this purpose may be subject to errors because the gas is invisible, extreme dilutions must be used, changes in temperature cause changes in volume, the gas is adsorbed on surfaces, and oxidation from sulfur dioxid to sulfur trioxid is relatively rapid.

The investigations indicate a point of general interest with reference to effects of the gas upon vegetation near industrial plants which emit sulfur dioxid from smokestacks. The relatively rapid oxidation of sulfur dioxid to sulfur trioxid confines the former to a rather small radius, limiting liability to injury to a more reduced area than is sometimes supposed; consequently the damage done to vegetation is likely to be very slight.

Conclusions

1. Methods of burning sulfur for experimental purposes are unsatisfactory, because of the production of sulfur trioxid and of sublimed sulfur.

2. Use of alcohol for the purpose of supplying heat, or of mixing with carbon bisulfide, is likely to result in the production of acetaldehyde. A chemical method is the most satisfactory one for obtaining the gas. Pure sulfur dioxid may be obtained from sodium bisulfite by the use of the method and apparatus here described.

3. Determinations of the concentration of sulfur dioxid at close intervals (15- or 20-minute intervals) is necessary because of the instability of the gas.

4. Decrease of the percentage of sulfur dioxid was found to be caused by absorption by plants and soil, adsorption on surfaces, oxidation from sulfur dioxid to sulfur trioxid, and probably other possibilities.

5. Oxidation from sulfur dioxid to sulfur trioxid is relatively rapid.

6. Adsorption and oxidation were found to be less active (*a*) in low temperatures than in high ones, so that higher percentages of sulfur dioxid were determined in high temperatures than in low ones; (*b*) in contact with paraffin than with glass surfaces. therefore the inside surface of the gas chamber was coated with paraffin; (*c*) as the degree of saturation of surfaces increased.

7. Rubber reduced an iodine solution used for determining the concentration of sulfur dioxid, resulting in an error in the determinations. This was found to be true though the rubber was not in contact with the solution. Therefore rubber stoppers may not be used in an analysis of the gas.

8. The content of the gas chamber was analyzed by drawing a sample of the mixture through an iodine solution in a series of absorption tubes with ground-glass stoppers, adapted for titration of excess iodine *in situ*, with a sodium thiosulfate solution.

9. The method developed was compared with that used by the Selby Smelter Commission in 1915, and was found to be more accurate for determining sulfur dioxid in dilutions needed for minimal injury to plants.

10. The advantages of the method are believed to be the following: (*a*) the glass surface, on which sulfur dioxid may be lost, is reduced to a minimum; (*b*) elimination of rubber near an iodine solution avoids reduction of iodine by that medium; (*c*) the method corrects for vapor pressure—a correction not made in previous methods.

11. The method is believed to be accurate to one part of sulfur dioxid in a million parts of air-gas mixture, and fairly accurate to two parts in ten million.

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EXPLANATION OF PLATE IX

Equipment for Experiments with Sulfur Dioxid

a, cylinder containing sodium hydroxid for testing sulfur dioxid.

b, tube to conduct sulfur dioxid from washing bottle, *h*, to testing cylinder, *a*.

c, *c'*, electric switches; *c* to motor for fan in gas chamber, *q*; *c'* to vacuum pump used for Selby method.

c'', wire connection and socket for vacuum pump.

d, sulfur dioxid generator, fitted with (1) separatory funnel for sulfuric acid, (2) outlet connected to aërating bulb in washing bottle, *h*, (3) outlet to first equilibrium flask, *g*.

e, water bath.

f, Bunsen burner.

g, *g'*, equilibrium flasks to control gas pressure in generator.

h, washing bottle containing distilled water saturated with sodium bisulfite and sulfur dioxid. Fitted with an inlet tube terminated with an aërating bulb, and with an outlet tube connected to the three-way stopcock, *i*.

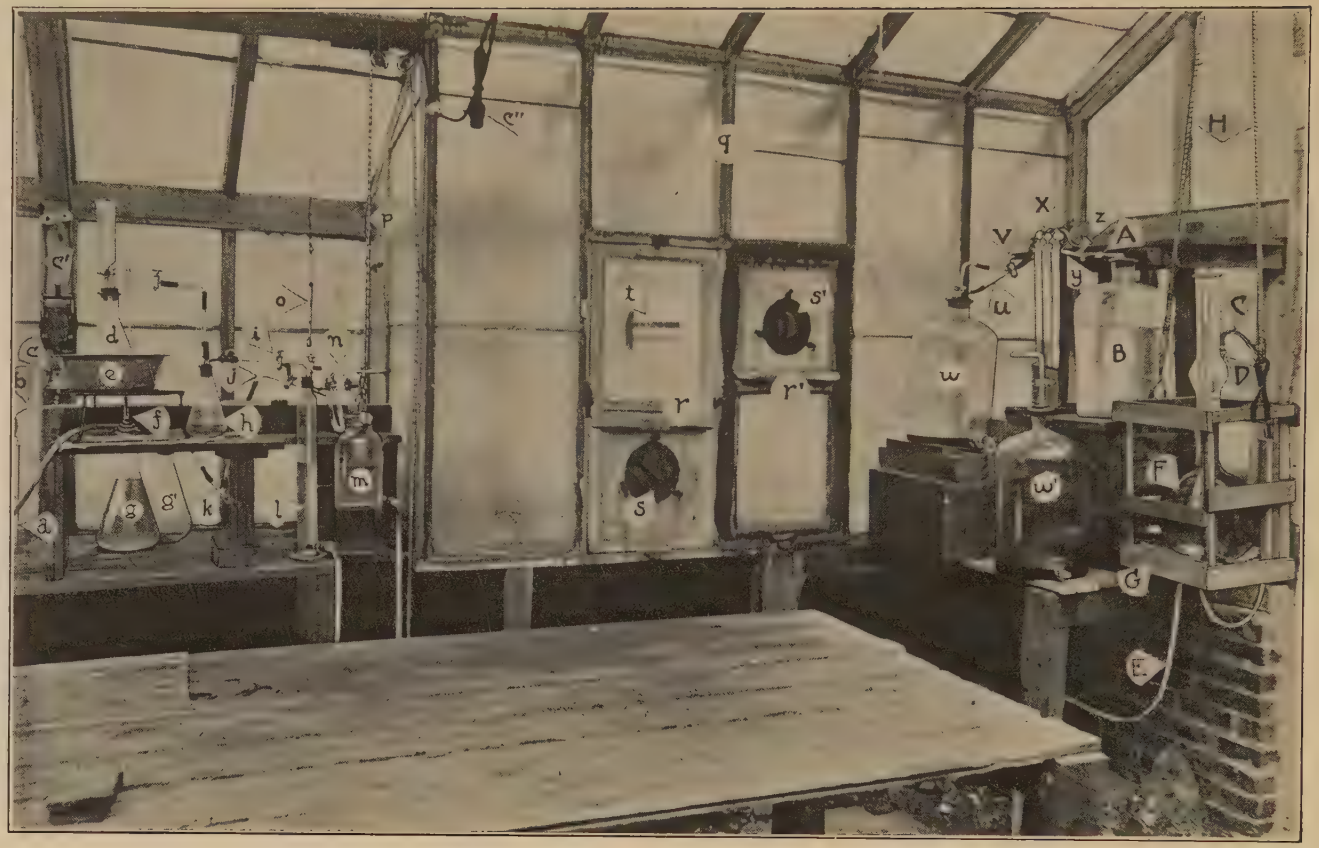
i, three-way stopcock from washing bottle, *h*, to collecting cylinder, *l*, and to a second three-way stopcock (seen at back of *i*). The second stopcock leads to tube *b* and to tube *j*, connected to the Y-tube, *k*.

j, tube from second three-way stopcock to one arm of the Y-tube, *k*.

k, Y-tube leading out of doors; one arm is connected to *j* from the second three-way stopcock (see *i*); the other arm is connected to the second equilibrium flask, *g'*.

l, sulfur dioxid-collecting cylinder, calibrated in cc., and containing distilled water saturated with sodium bisulfite and sulfur dioxid; three openings: (1) inlet from three-way stopcock, *i*, (2) outlet, *n*, to gas chamber, *q*, and (3) outlet at bottom connected to leveling bottle, *m*.

m, leveling bottle, connected to collecting cylinder, *l*; it contains distilled water saturated with sodium bisulfite and sulfur dioxid. Two openings at the top: (1) vertical tube to carry and control rise of water due to sudden flow of gas into the collecting cylinder, *l*; (2) outlet to two U-tubes in series. The first U-tube contains mercury, the second sodium hydroxid.



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n, outlet tube with stopcock, from collecting cylinder, *l*, to chamber, *q*.

o, thermometer to determine temperature of sulfur dioxid when sent into chamber.

p, rope-and-pulley system; weight attached to rope is not shown in the plate.

q, gas chamber in which experimentation was carried on. Electric fan and wet-and-dry bulb psychrometer are within the chamber.

r, *r'*, closely-fitting doors: *r*, unsealed, so that it may be removed; *r'*, sealed.

s, *s'*, removable discs closely fitting into openings, which are further sealed with sheet rubber.

t, space cleared of paraffin coating on inner surface, for window purposes.

u, outlet from gas chamber to three-way stopcock, *v*.

v, three-way stopcock from chamber, *q*, to semi-evacuated aspirator, *w*, and to absorption tubes, *x*.

w, 12-liter aspirator containing starch iodid solution; evacuated to 380 mm. pressure.

w', control, or "blank" aspirator, containing starch iodid solution at 760 mm. pressure.

x, series of three absorption tubes (see text fig. 4). The first two tubes contain iodine solution, the third contains starch solution.

y, tube (with stopcock not shown) from stopcock, *v*, to T-tube, *A*, leading to the aspirator, *B*; *y* is used to wash air out of the system.

z, stopcock between the absorption tubes, *x*, and the T-tube, *A*.

A, T-tube from wash tube, *y*, and from absorption tubes, *x*, to the aspirator, *B*.

B, aspirator containing water which is tapped in order to draw the sample of gas mixture from the chamber. Inlet at top from T-tube, *A*; two outlets below: (1) to tube *C*, (2) to tube *E*.

C, rubber tube connecting aspirator, *B*, to measuring flask, *F*.

D, lip on bulb for inlet tube connected to the aspirator.

E, outlet from the aspirator, for water not measured; used when washing air from the system.

F, measuring flask, calibrated in cc.; tall neck, with bulb, for leveling purposes; the inlet tube, from *D*, reaches to the bottom of the flask.

G, crate for *F*.

H, rope-and-pulley system connecting crate, *G*, to weight (not shown in the plate) for the purpose of moving the measuring flask.